Chapter 2
Mercury Study Overview

2.1 Mercury Introduction

2.1.1 Physical/Chemical Properties

Mercury is a naturally occurring transition metal, in Group II of the periodic table, along with zinc and cadmium. The atomic number for mercury is 80 and its atomic weight is 200.59 g/mole. Mercury is the only metal that occurs in a liquid state at typical environmental temperatures. The melting point of mercury is -39.87 °C, and its boiling point is 356.58 °C. Mercury has a density of 13.59 g/cm^3 and a vapor pressure of 0.00185 mm at 25 °C.

The solubility of mercury in water is approximately 0.28 µmoles/L (56.2 µg/L) at 25 °C. Its electrical resistivity is 95.76 µohm-cm at 20 °C, making it an excellent electrical conductor. In fact, the value of the ohm is formally defined on the basis of the resistance of a column of mercury of specific dimensions.

Mercury occurs naturally in the environment with three possible valences, or oxidation states, Hg^0, Hg^{+1}, and Hg^{+2}. The principal mineral source of mercury in the geosphere is cinnabar (HgS). Mercury is extracted from this ore by roasting in an oxygen atmosphere to produce elemental mercury, which can be further purified by distillation. Mercury also occurs as a trace element in other commercially significant geologic deposits, including coal.

The reduction potential is 0.851 volts for the reaction:

$$Hg^{+2} + 2e^- \leftrightarrow Hg^0$$

and 0.796 volts for the reaction:

$$Hg_2^{+2} + 2e^- \leftrightarrow 2Hg^0$$

placing mercury higher on the redox scale than most other metals.

2.1.2 Mercury Production, Uses, and Releases

Because it is a dense liquid at typical environmental temperatures and responds in a predictable fashion to changes in temperature and pressure, elemental mercury is commonly used in barometers and thermometers. Its high reduction potential and low resistivity make it ideal for use in battery cells, electrical switches, and fluorescent lamps.

Elemental mercury is also used as a catalyst in the oxidation of organic compounds and the production of chlorine and caustic soda. Elemental mercury is a principal component of the silver amalgam used in dental fillings. Mercury may be used in gold mining operations because it forms an amalgam with gold which then can be separated from the gold-bearing ore. It has been used in chlor-alkali plants around the world. Historically, mercury compounds have been used in medicinal products, including topical disinfectants such as Mercurochrome, and as a preservative in some vaccines and cosmetics. For many years, mercuric chloride was used as a biocide to preserve water samples collected for analyses of other environmental contaminants. Mercury compounds were used for many years as antifungal agents in interior and exterior paints and at pulp and paper mills.

According to the U.S. Geological Survey (USGS), there have been no domestic mines producing mercury as a primary product since 1990 (USGS, 1999). Virtually all domestic mercury production involves recovery or recycling of mercury from secondary sources such as spent batteries, mercury-containing lamps, switches, dental amalgams, and wastes from laboratories and electrolytic processes.

Data from USGS for the period from 1995 to 1999 indicate that domestic production of mercury (from secondary sources), as well as imports and exports of mercury, and industrial consumption of mercury declined. In addition, world-wide mine production declined by approximately 40% over the same period, from 3,190 to 1,970 metric tons. USGS estimated that domestic industrial consumption of mercury in 1997 was 346 metric tons (762,800 pounds). Data from EPA's Toxics Release Inventory (TRI) for 1997 indicate that 73,334 pounds of mercury (≈10% of domestic production) were released to the environment by facilities that were required to report releases to EPA. According to USGS, electrolytic production of chlorine and caustic soda account for roughly half of the domestic use of mercury, with electrical applications and products accounting for another 25%.

Global releases of mercury to the environment come from both natural and anthropogenic (caused by human activity) sources. Many of these sources are the result of releasing geologically bound mercury to the atmosphere. Once mercury enters the atmosphere, it becomes part of a global cycle of mercury among land, water, and the atmosphere. In its 1997 Report to Congress on mercury, EPA estimated that the global mercury cycle involved the release of 5,500 metric tons (12,130,000 pounds) of mercury to the atmosphere from all natural and anthropogenic sources world-wide (USEPA, 1997b). Of that total, EPA estimated that 158 metric tons (348,300 pounds) were contributed from anthropogenic sources in the U.S. in 1994 - 1995, representing about 3% of the total global mercury input to the atmosphere. Of that 158 metric tons, approximately 87% came from combustion sources, and approximately 10% came from manufacturing sources. A breakdown of these 1994 - 1995 anthropogenic emission estimates includes:

- Combustion sources (87%)
  - Coal-fired utility boilers (32.6%)
  - Municipal waste combustors (18.7%)
  - Commercial/industrial boilers (17.9%)
  - Medical waste incinerators (10.1%)
  - Hazardous waste combustors (4.4%)
  - All other combustion sources (3.3%)
- Manufacturing sources (10%)
  - Chlor-alkali plants (4.5%)
  - Portland cement kilns - excludes those that burn hazardous waste (3.1%)
  - All other manufacturing sources (2.4%)

Although it does not involve quantities of mercury similar to those used on an industrial scale, elemental mercury is used in various cultural and religious practices of some Caribbean and Latin American immigrants to the U.S., which may result in exposures that exceed current occupational standards (Riley, *et al.*, 2001). Frequently reported uses of mercury in such practices include those designed to bring luck or ward off evil by:

- Carrying a capsule, vial, or pouch containing elemental mercury on one's person
- Sprinkling it in a home or car
- Mixing it with perfume
- Burning a candle laced with mercury

Elemental mercury has also been used as a folk medicine treatment for gastroenteritis among some Mexican Americans.

In another study of such cultural and religious practices, Johnson (1999) reported that 64% of the mercury users in that study in New York City dispose of mercury by throwing it in the trash, 27% flushed used mercury down the toilet, and 9% disposed of mercury outdoors. Therefore, although the overall quantities of mercury used in these cultural practices may pale in comparison to industrial uses, the uncontrolled disposal practices could make such cultural uses significant sources of mercury to local environments.

2.1.3 Regulatory Background

Efforts in the U.S. to regulate releases of mercury to the environment began shortly after the formation of EPA in 1970. EPA regulates mercury under a wide range of environmental statutes. By 1976, the Office of Water listed mercury as one of the 129 pollutants in the consent decree that resulted from *NRDC v. Train (8 ERC 2120, 1976)*. As a result, mercury is regulated in effluent guidelines developed under the Clean Water Act and administered through the National Pollutant Discharge Elimination System (NPDES). The Office of Water has established water quality criteria (WQC) for freshwater and marine systems. The freshwater chronic WQC is 0.012 µg/L of mercury. The freshwater acute WQC is 2.1 µg/L. The WQC for human health is 0.05 µg/L.

Under the Safe Drinking Water Act, EPA established a maximum contaminant level (MCL) of 2 µg/L in 1992. Under the auspices of the Resource Conservation and Recovery Act (RCRA), EPA placed mercury on Appendix VIII (hazardous substances) and Appendix IX (groundwater monitoring), and established a Universal Treatment Standard (UTS) of 25 µg/L of mercury in non-wastewaters when subjected to the toxicity characteristic leaching procedure (TCLP) and 150 µg/L in wastewaters. Mercury is included in the Toxics Release Inventory (TRI) developed under the Emergency Planning and Community Right to Know Act (EPCRA).

The use of mercury in paints was discontinued in 1991 under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). Registrations of the last two mercury-based pesticides (Calochlor and Calogran) were voluntarily cancelled by the manufacturer in 1993. In 1996, Congress enacted the Mercury-Containing and Rechargeable Battery Management Act to phase out the use of mercury in batteries. The Act limits the mercury content of "button" batteries to 25 mg per battery, prohibits the sale of most other types of batteries containing mercury, and requires that manufacturers identify suitable recycling facilities for any mercuric-oxide batteries it sells.

Mercury and mercury compounds are classified as hazardous air pollutants (HAPs) under the Clean Air Act, and EPA has established national emission standards for mercury in five source categories: ore processing facilities, mercury cell chlor-alkali plants, sewage sludge drying operations, municipal waste combustors, and medical waste incinerators.

Discharges of mercury have been significantly limited under the Great Lakes Initiative (GLI), in recognition of the impact of mercury on the Great Lakes ecosystem and the associated effects on human health in the region. In 1995, EPA issued GLI guidance that recommends that a water quality criterion of 1.8 ng/L (0.0018 µg/L) for dissolved mercury for the protection of human health (FR Vol. 60 No. 56, March 23, 1995, pp. 15366-15425).

Under the Federal Food, Drug, and Cosmetic Act, the Food and Drug Administration (FDA) banned most uses of mercury in over the counter medications and limited the concentrations of mercury used as preservatives in eye-area cosmetics. The FDA also regulates the use of mercury in dental amalgams, classifying the silver-mercury alloy as a Class II medical device, thereby subjecting it to additional controls and imposing safety regulations on its use and disposal.

2.1.4 Fate and Effects

Unlike synthetic organic contaminants, mercury is a naturally occurring element, and therefore it cannot be created or destroyed by chemical, biological, or physical processes. Rather, mercury can be transformed by oxidation or reduction reactions, or it can combine with other elements to form inorganic or organic mercury compounds. The organomercury compounds are characterized by a covalent bond between the mercury atom and a carbon atom, making mercury unusual among metals (but not unique), in that many metals form only ionic bonds with other elements.

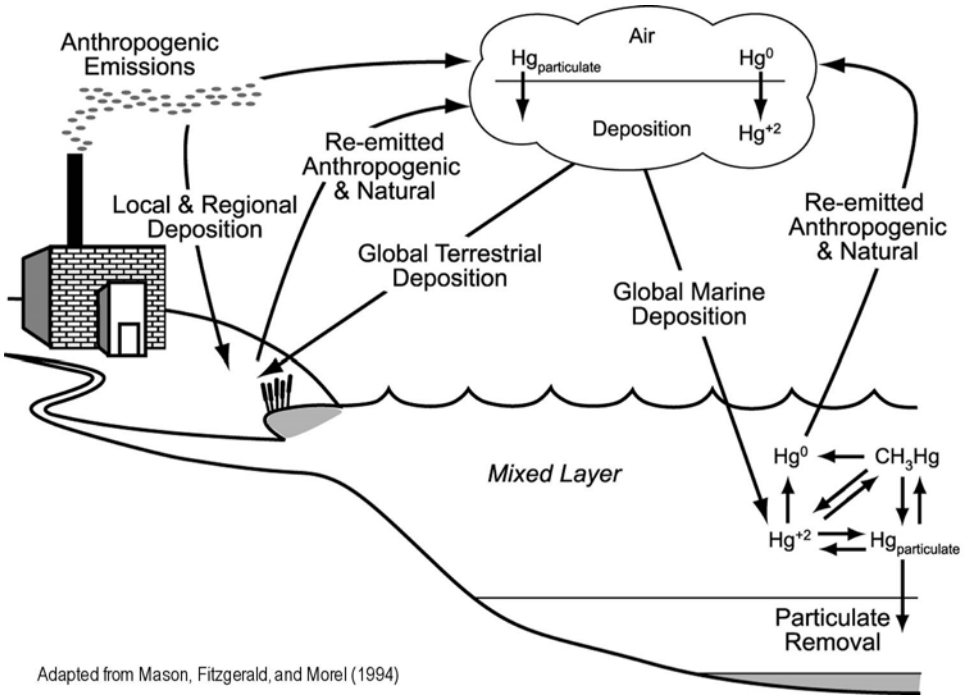
The following are the mercury compounds most likely to be found under environmental conditions: mercuric chloride ($HgCl_2$), mercuric hydroxide (Hg $[OH]_2$), mercuric sulfide (HgS), methylmercuric chloride (CH_3HgCl), methylmercuric hydroxide (CH_3HgOH), and dimethyl mercury ($[CH_3]_2Hg$) (USEPA, 1997b).

Due to the volatility of elemental mercury, the atmosphere is both an important reservoir and a major component of the global mercury cycle. That global cycle encompasses the flux of mercury in its many forms to and from the atmosphere, fresh and marine water bodies, and the land. The cycle includes a natural component that is the result of mercury that originated in geologic deposits and that has been released from those deposits by natural processes. The cycle has been significantly perturbed or modified by human activities, and includes both regional and local sources and sinks of various forms of mercury.

Although a detailed discussion of the global mercury cycle is beyond the scope of this report, in general terms, the cycle (Figure 2-1) is characterized by the following exchanges and transformations of mercury:

- Volatilization from land-based sources to the atmosphere
- Volatilization from marine-based sources to the atmosphere
- Deposition from atmosphere to land, oceans, and other water bodies
- Anthropogenic inputs of gaseous and particulate forms of mercury to the atmosphere from combustion processes and municipal and industrial sources on land
- Run-off of natural and anthropogenic mercury from land to freshwaters and oceans
- Exchanges between dissolved and particulate forms of mercury in oceans and lakes
- Exchanges of mercury between inorganic and organic forms in the water and sediments of oceans and lakes
- Deposition of mercury in sediments of oceans and lakes
- Local and regional deposition of mercury from anthropogenic combustion sources and municipal and industrial sources

Figure 2-1. Global Mercury Cycle



The residence time of elemental mercury in the atmosphere is estimated to be about one year (EPA, 1997b). As a result, mercury entering the atmosphere from any given source may be distributed globally, making mercury a ubiquitous contaminant.

2.1.5 Biological Transformations

Mercury enters the food web primarily through aquatic systems, where it is associated with dissolved and particulate forms of organic carbon (DOC and POC), and where it may undergo methylation by bacteria in sediments or in the water column to form methylmercury (USEPA, 1997b). Methylmercury accumulates in the tissues of aquatic organisms and methylmercury concentrations are magnified in aquatic food webs, with highest concentrations often found in the top predators, including many game fish. As a result, human exposure pathways related to terrestrial plants and grazing animals are much less important than pathways related to consumption of fish (USEPA, 1997b).

2.1.6 Toxicity

The effects of mercury exposure on organisms depend on the route of exposure and the form of mercury. Many people are familiar with the "Mad Hatter" in Lewis Carroll's "Alice in Wonderland," whose madness described the results of exposure of hatmakers to the mercuric nitrate used to shrink felt for hats. While the etymology of the expression "mad as a hatter" is apparently subject to some debate, the effects of exposure to elemental mercury vapors and/or soluble mercury salts were documented at the time. The "Danbury shakes" was the name given to the neurological effects exhibited by hatmakers in Danbury, Connecticut, in the 19th century.

Whether the route of exposure is through inhalation, dermal exposure, ingestion of food, or other means, mercury and mercury compounds are readily transported throughout humans and animals by blood circulation. Elemental mercury dissolved in the blood can cross the blood/brain barrier, where it can accumulate in nerve tissue. Symptoms of chronic exposure to mercury vapors include: excitability,

confusion and mental instability, personality changes, and fine tremors in the extremities. Mercury can cause kidney damage, as the kidneys works to remove mercury from the bloodstream.

The effects of organomercury compounds, particularly methylmercury and dimethylmercury, are more severe than for elemental mercury, given equivalent exposures or doses. Methylmercury is known to have teratogenic effects in the children of mothers exposed to this organomercury compound. Mild maternal exposures cause mainly neurological effects in the children, including developmental delays, reduced intelligence, and altered muscle reflexes.

Much of the data on the direct effects of elemental and organomercury exposure are the result of studies of long-term exposures of the people living around Minamata Bay, on the western coast of Kyushu, in Japan. Beginning in 1956, a series of patients were identified as exhibiting symptoms of severe convulsions, intermittent loss of consciousness, altered mental state, and ultimately permanent coma and death. The common link among the patients was that they consumed large quantities of fish from Minamata Bay. A second outbreak of what became known as "Minamata disease" occurred in 1965 when patients with the same symptoms were identified near Niigata City, far from Minamata. The affected individuals were all fishermen living along the Agano River. In these cases, methylmercury was identified in both the local fish that the patients consumed as well as in tissues from the patients' bodies.

Ultimately, the Japanese government publicly acknowledged that Minamata disease resulted from environmental pollution. The source of the pollution in Minamata Bay was the untreated effluent from the Nippon Chisso chemical manufacturing plant in Minamata City. Nippon Chisso produced acetaldehyde and polyvinyl chloride (PVC) at the Minamata plant, and used large quantities of inorganic mercury compounds as reaction catalysts. Although most of the mercury was recovered within the plant, massive amounts were discharged in the wastewater over a period of decades, and much of it accumulated in the sediments and biota of the bay. The methylmercury found in fish from the Agano River was ultimately traced to the Showa Denko Company facility in Kase, on the upper reaches of the river (Ui, 1992).

The extreme toxicity of dimethylmercury came to the attention of the scientific community most recently as the result of a tragic laboratory accident. In August 1996, Dr. Karen Wetterhahn, working at Dartmouth College, was exposed to approximately 400 milligrams of dimethylmercury when a few drops of a standard she was using to calibrate a nuclear magnetic resonance instrument accidentally spilled on the back of her latex glove. The spill occurred in a hood and she cleaned up the spill and removed the glove. Five months after the accident, she was admitted to the hospital exhibiting problems with her speech, balance, and gait. Twenty-two days after the onset of these neurological symptoms, she did not respond to visual or verbal stimuli, and lapsed into a coma. She died in June 1997, almost 300 days after the accident (Nierenberg *et al.*, 1998).

2.2 Study Design

2.2.1 Description

Mercury was chosen for inclusion in the LMMB Study as a representative of persistent, bioaccumulative metals. Mercury was measured in vapor, precipitation, particulates, atmospheric dry deposition, water in the open lake, tributaries, sediment, lower pelagic food web organisms, and top predator fish. The data generated from this study were used to estimate an overall mass balance of mercury in Lake Michigan (see Section 1.4). In addition, methylmercury was determined in tributary samples.

2.2.2 Scope

To develop a mass balance for mercury in Lake Michigan, all significant sources and stores of mercury in the environment were measured. Significant sources and stores included tributary inputs, atmospheric inputs from the vapor phase, particulate phase, and precipitation, sediment, lower pelagic food web organisms, and fish. The specific components that were studied are shown in Table 2-1.

Field sampling was conducted from February 1994 through October 1995, with an additional sampling cruise in May 1996 to retrieve sediment traps and collect samples at stations LM94-11, LM94-17, LM94-18, LM94-21S and LM94-32.

2.2.3 Organization/Management

The responsibility for collecting and analyzing mercury samples from the various components was divided among six principal investigators (PIs, see Table 2-1). Each principal investigator developed a quality assurance project plan (QAPP) that was submitted to EPA's Great Lakes National Program Office (GLNPO) for approval. The QAPPs detailed the project management, study design, and sampling and analysis procedures that would be used in the study and the quality control elements that would be implemented to protect the integrity of the data. The LMMB quality assurance program is further discussed in Section 2.6, and detailed information on the quality assurance activities and data quality assessment specific to each ecosystem component are discussed in Chapters 3 through 8.

Table 2-1. Components Sampled by Principal Investigators

Ecosystem Compartment	Component	Principal Investigator
Atmosphere	Vapor Particulate Precipitation	Gerald Keeler, Ph.D., University of Michigan School of Public Health Environmental Health Sciences
Tributary	Dissolved Mercury and Methylmercury Total Mercury and Methylmercury	James Hurley, Ph.D., University of Wisconsin Water Science and Engineering Laboratory
Open Lake	Particulate matter Total mercury	Robert Mason, Ph.D., University of Maryland Chesapeake Biological Laboratory
Sediment	Surficial sediment Resuspended sediment	Ronald Rossmann, Ph.D., USEPA Large Lakes Research Station
Lower Pelagic Food Web Organisms	Zooplankton Phytoplankton	Edward Nater, Ph.D., University of Minnesota Department of Soil, Water, and Climate
Fish	Lake Trout Coho Salmon	Jerome Nriagu, Ph.D., University of Michigan Department of Environmental Health Sciences School of Public Health

2.3 Sampling Locations

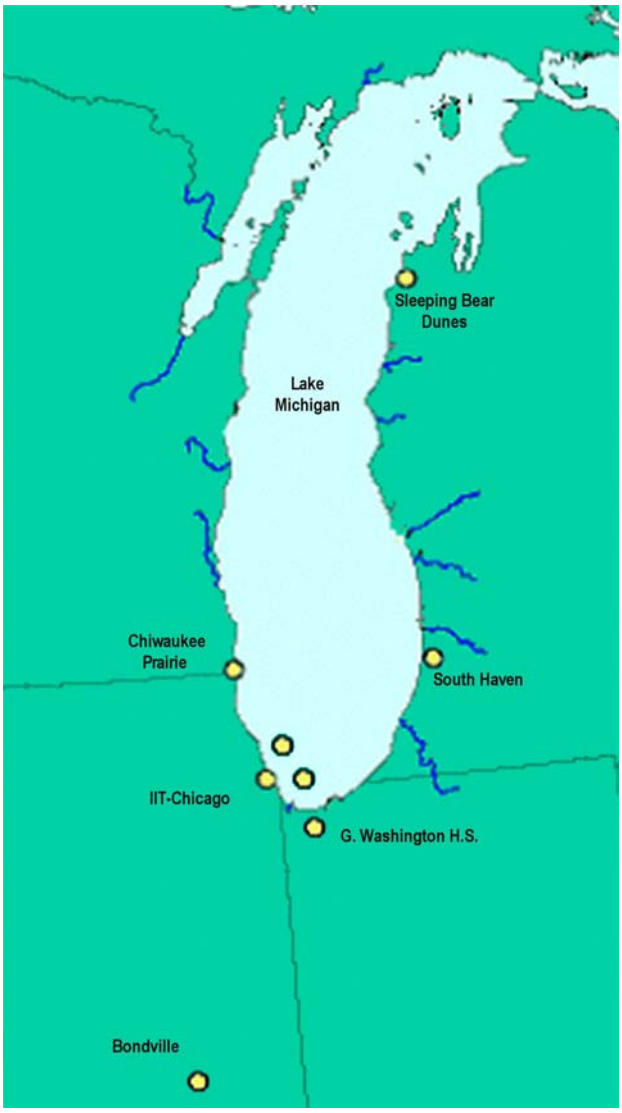
2.3.1 Atmospheric Components

Atmospheric samples were collected at five shoreline sampling stations and two open-lake sampling stations within Lake Michigan (Figure 2-2). One of the shoreline sampling stations (George Washington High School in Chicago) was used only once over the course of the study. In addition, one out-of-basin land-based sampling station was established as a regional background site to represent air coming over Lake Michigan during periods of southwest or northwest prevailing winds. The sampling locations and sampling frequencies for the LMMB Project were selected through discussions with experts in the field

during several workshops, including the Great Lakes Mass Balance Planning Workshop in April 1992 and the LMMB Planning Meeting in September 1993. Site-selection criteria considered predominant annual wind directions, source areas, and episodic summer events.

In general, sites were selected to be regionally representative of land-use categories and to represent the different potential sources of pollutants in this study (e.g., releases associated with population centers versus agricultural areas).

Figure 2-2. Atmospheric Sampling Stations



The shoreline atmospheric sampling stations include those specific to the LMMB Study as well as several that are part of the Integrated Atmospheric Deposition Network (IADN). Samples were collected from the land-based IADN stations at Sleeping Bear Dunes and Bondville from April 1994 through October 1995. Sampling at these IADN stations was governed by study design and quality assurance programs specific to IADN, but generally similar to those in the LMMB Study, so the data have been incorporated into the LMMB database. The locations of the shoreline atmospheric mercury sampling stations are shown in Figure 2-2.

Atmospheric samples were collected from the *R/V Lake Guardian* at two stations (Fig. 2-2) in the open lake in July 1994 and January 1995. However, because of the limited spatial and temporal coverage represented by these open-lake atmospheric samples, they were not included in the LMMB Study data set, nor are they discussed in this report.

For vapor and particulate samples, one 24-h composite sample was collected every 6 days using automated sampling equipment. Precipitation samples were collected by automated equipment that sensed the presence of precipitation and collected samples from each precipitation event during April through October. Precipitation samples collected in November through March were collected on a weekly basis (e.g., each sample represented the precipitation that fell during all of that week). These frequencies were generally followed as sampling schedules permitted and except in cases of sampler malfunction, lack of precipitation, or when circumstances prevented retrieval of a sample.

2.3.2 Tributaries

Tributary samples were collected from 11 rivers that flow into Lake Michigan (Figure 2-3). These tributaries included the Menoninee, Fox, Sheboygan, and Milwaukee Rivers in Wisconsin; the Grand Calumet River in Indiana; and the St. Joseph, Kalamazoo, Grand, Muskegon, Pere Marquette, and Manistique Rivers in Michigan. With the exception of the Pere Marquette River, these tributaries were selected for the LMMB Study because of elevated concentrations of contaminants in resident fish. The Pere Marquette River was selected because it has a fairly large and pristine watershed.

The 11 monitored tributaries represent greater than 90% of the total river flow into Lake Michigan and an even higher percentage of the total tributary load of pollutants into Lake Michigan. Samples collected from the Pere Marquette River can be used to estimate loads from the small portion of the Lake Michigan watershed that was not monitored in this study.

Table 2-2 describes specific watershed characteristics and impairment information for each of the monitored tributaries. Of the 11 tributaries, 6 (the Kalamazoo, Manistique, Menominee, Fox, Sheboygan, and Grand Calumet Rivers) are classified as Great Lakes areas of concern (AOCs). Areas of concern are severely degraded geographic areas within the Great Lakes Basin. They are defined by the US-Canada Great Lakes Water Quality Agreement (Annex 2 of the 1987 Protocol) as "geographic areas that fail to meet the general or specific objectives of the agreement where such failure has caused or is likely to cause impairment of beneficial use or the area's ability to support aquatic life." Most of the 11 tributaries are also listed on the Clean Water Act Section 303(d) list of impaired water bodies due to contamination from mercury, PCBs, and other pollutants.

Figure 2-3. Tributary Sampling Stations

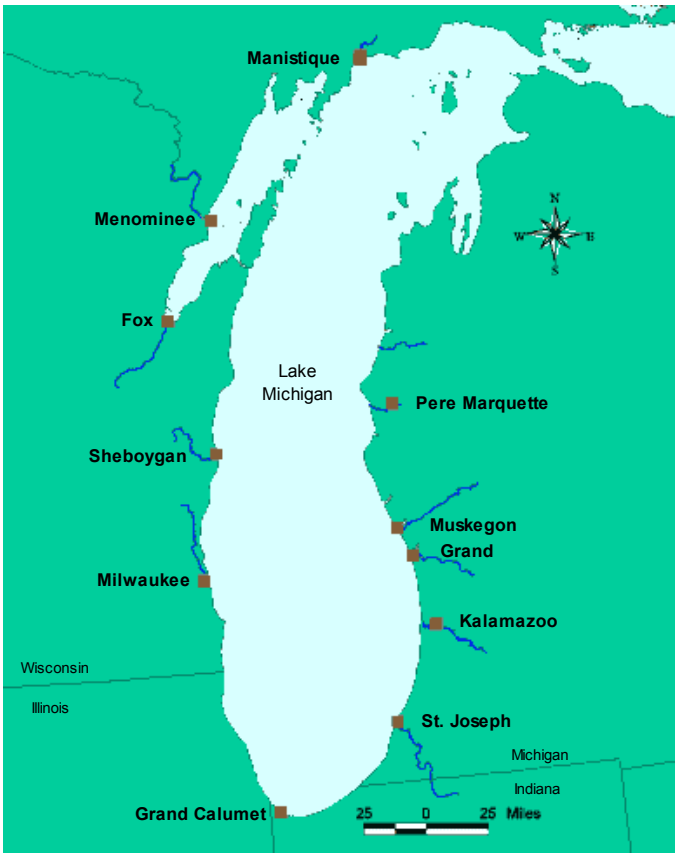


Table 2-2. Watershed Characteristics for Tributaries Monitored in the LMMB Study

Tributary	Watershed area (mi^2)	Total river miles in watershed	Riparian Habitat		IWI Score[a]	Impaired for[b]	Area of Concern
			Forested	Agricultural/ Urban			
St. Joseph	4685	3743	25-50%	>50%	3 - less serious problems, low vulnerability	*E. coli*, mercury, PCBs, pathogens, macro-invertebrate community	
Kalamazoo	2047	1560	25-50%	>50%	3 - less serious problems, low vulnerability	Mercury, PCBs	X
Grand (lower)	2003	2014	25-50%	>50%	5 - more serious problems, low vulnerability	PCBs, pathogens	
Muskegon	2686	1886	25-50%	>50%	5 - more serious problems, low vulnerability		
Pere Marquette	2644	1356	25-50%	>50%	3 - less serious problems, low vulnerability	Mercury, PCBs	
Manistique	1464	1061	>75%	20-50%	1 - better quality, low vulnerability	Mercury, PCBs, pathogens	X
Menominee	2306	1660	>75%	20-50%	1 - better quality, low vulnerability	Dioxin, PCBs, mercury, pathogens	X
Fox (lower)	442	700	25-50%	>50%	6 - more serious problems, high vulnerability	PCBs, organic enrichment, dissolved oxygen	X
Sheboygan	2201	1699	25-50%	>50%	5 - more serious problems, low vulnerability	PCBs, mercury	X
Milwaukee	864	802	25-50%	>50%	5 - more serious problems, low vulnerability	PCBs	
Grand Calumet	1039	760	25-50%	>50%	5 - more serious problems, low vulnerability	PCBs, pesticides, lead, mercury, dissolved oxygen, cyanide, chlorides, impaired biotic community, oil and grease, copper	X

[a]EPA's Index of Watershed Indicators Score for assessing the health of aquatic resources.
[b]Based on 1998 listing of Clean Water Act Section 303(d) impaired waters.

2.3.3 Open Lake

Open-lake water column samples were collected from 17 sampling locations on Lake Michigan, one sampling location in Green Bay, and one sampling location on Lake Huron (Figure 2-4). Open-lake samples were collected during six cruises of the *R/V Lake Guardian* between June 1994 and September 1995. The dates of the six cruises are shown in Table 2-3.

Figure 2-4. Open-Lake Water Column Sampling Stations

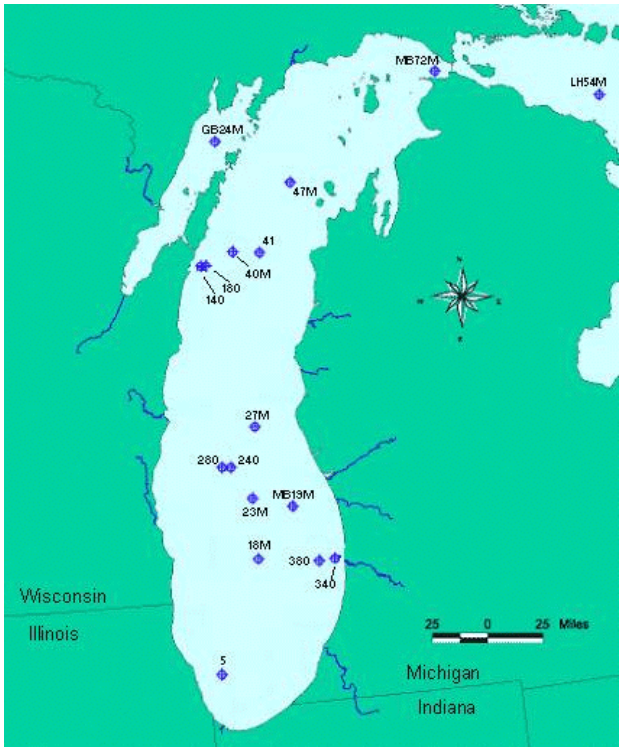


Table 2-3. Open-lake Cruise Dates

Cruise Date
June 1994
August 1994
October/November 1994
March/April 1995
August 1995
September/October 1995

The first cruise during which mercury samples were collected was in early summer (June 1994), after the onset of stratification. The second and third surveys were in late summer (August 1994) and fall (October 1994), during later stages of stratification. The fourth survey was conducted in March 1995, during non-stratified conditions. The fifth and sixth surveys occurred in August and September 1995, during stratification.

During stratification, samples were collected from two or three depths to represent the epilimnion and the hypolimnion. When the water column was unstratified, samples at some stations were collected from mid-depth, while at other stations, samples were collected from two depths.

2.3.4 Sediment

In 1994, 1995, and 1996, sediment samples were collected from Lake Michigan by box coring, Ponar grabs, and gravity coring. The location of the sediment sampling stations and the sampling device used are shown in Figure 2-5. The sediment sampling locations were selected to help define the three depositional zones (depositional, transitional, and non-depositional).

In addition to grab samples of sediments, sediment traps were deployed at eight locations in Lake Michigan (see Figure 2-6). The trap at Station 3, excluded from the figure but located in northern Lake Michigan, was lost. Samples from the two traps at Station 6 had mercury chloride added as a preservative to their collection bottles prior to deployment and therefore were not analyzed. The trap placed at a depth of 245 m at Station 5 failed, and no sample was available from the trap at Station 4. Enough sample was available for mercury analysis from Stations 1, 2, 5, 7, and 8. Samples from two depths were available from Stations 7 and 8.

Figure 2-5. Locations of Sediment Cores

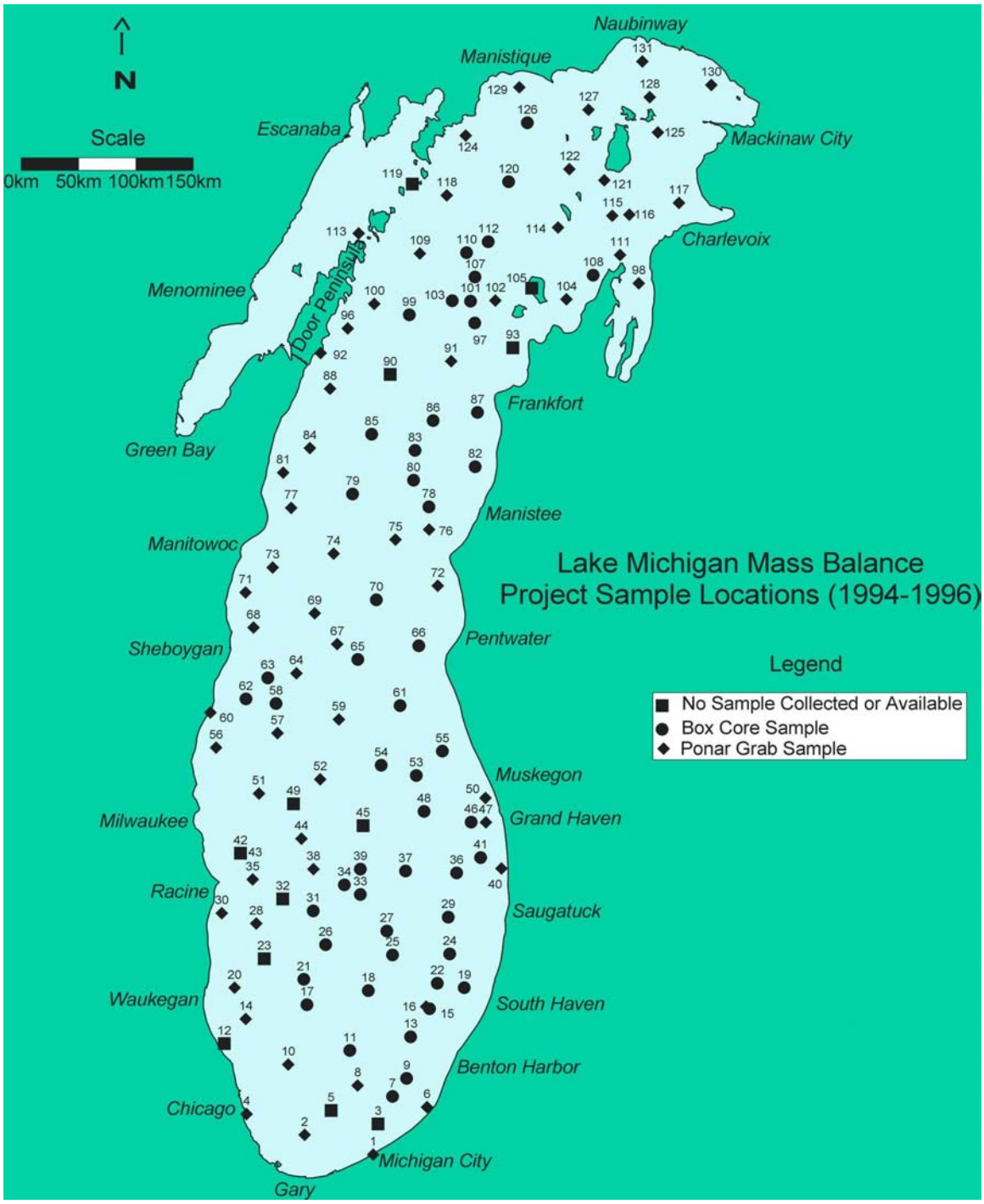
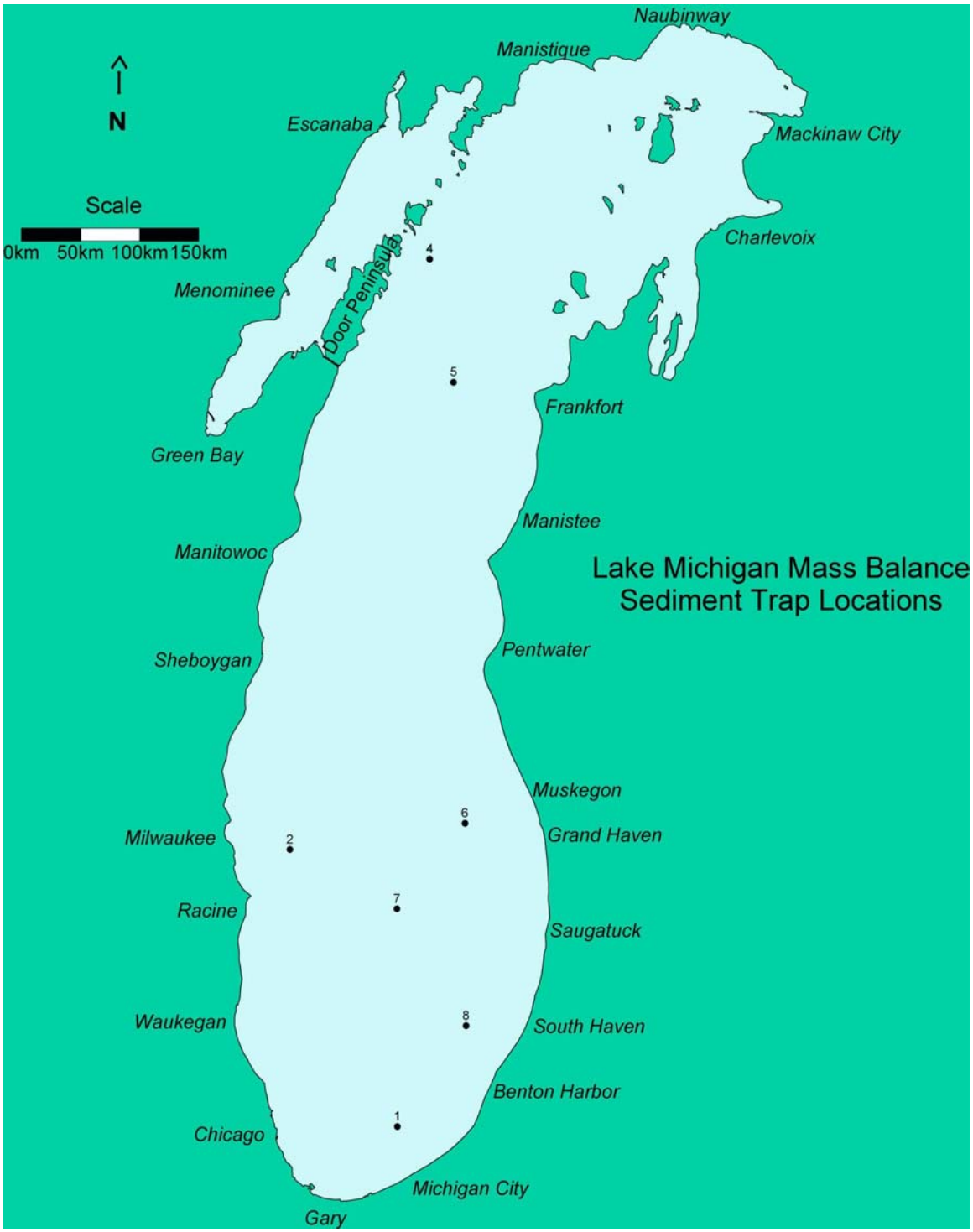


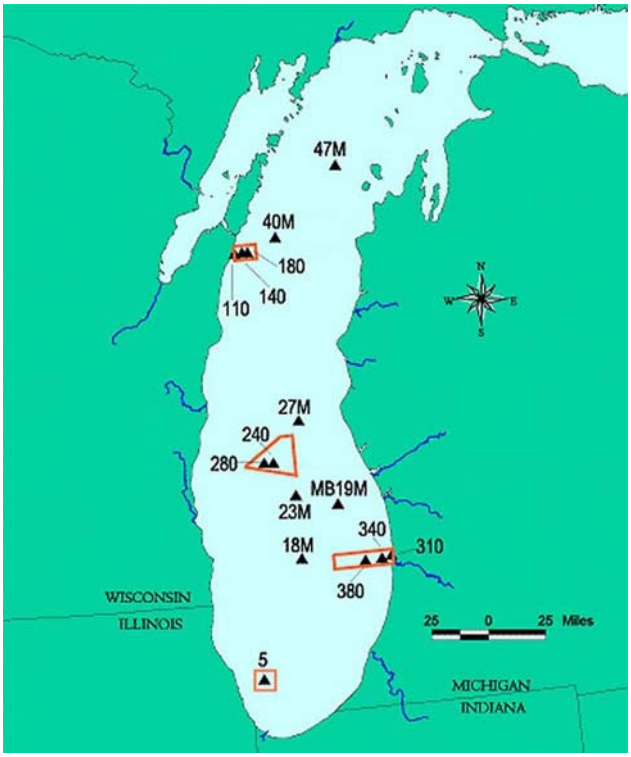
Figure 2-6. Sediment Trap Locations



2.3.5 Lower Pelagic Food Web Organisms

Plankton samples were collected from 12 stations in Lake Michigan selected by GLNPO and the PIs in advance of sampling (Figure 2-7). The stations included eight stations in three biological sampling areas or "biota boxes" (Stations 110, 140, 180, 240, 280, 310, 340, and 380), three master stations (18M, 27M, and 47M), and a fourth biota box centered around Station 5, near Chicago. The four biota boxes are outlined in red in Figure 2-7. Samples were collected on several occasions, from June 1994 to September 1995.

Figure 2-7. Sampling Stations for Lower Pelagic Food Web Organisms and Fish



In addition, zooplankton samples were collected from Station 10M in January 1995 and phytoplankton samples were collected from Stations 23M and 41 in June 1994. A total of 72 zooplankton and 71 phytoplankton samples were collected during the study.

2.3.6 Fish

Lake Michigan fish were collected from April 1994 through October 1995 for total mercury analysis. Lake trout and coho salmon were collected using gill nets, trawl nets, or other appropriate means (Table 2-4). Up to five individual fish of the same species and size or age category were combined to produce composite fish samples at each collection. In total, 693 adult lake trout from 172 to 933 mm in length were collected from three of the four biological sampling areas or biota boxes shown in Figure 2-7 (fish were *not* collected from the biota box at Station 5, near Chicago):

- **Sturgeon Bay biota box** — a series of three nearshore stations (110, 140, and 180) on the western side of the northern Lake Michigan basin near Sturgeon Bay, Wisconsin
- **Port Washington biota box** — a series of two mid-lake reef stations (240 and 280) in the central Lake Michigan basin near Port Washington, Wisconsin
- **Saugatuck biota box** — a series of three nearshore stations (310, 340, and 380) on the eastern side of the southern Lake Michigan basin near Saugatuck, Michigan

Table 2-4. Number of Fish Collected by Technique

Species	Number of Fish Collected by Technique				
	Hook and Line	Gill Net	Bottom Trawl	Harvest Weir	Dip Net
Lake Trout	—	666	27	—	—
Coho salmon — adult	135	3	—	—	—
Coho salmon — yearling	29	—	—	9	—
Coho salmon — hatchery	—	—	—	—	25

These fish were used to prepare 156 trout composite samples that were analyzed for total mercury by cold vapor atomic fluorescence spectroscopy (Table 2-5).

A total of 201 coho salmon were collected in three distinct age classes (hatchery, yearlings, and adult). Of the 201 fish, 138 were adult coho salmon collected from 54 sites selected to follow the seasonal migration of coho, which travel up Lake Michigan tributaries in the fall to spawn. During the summer, coho salmon were collected from the east central and west central regions of the lake. During the fall, coho salmon were collected from the northeastern side of the lake near the Platte River and on the western side of the lake near the Kewaunee River. These 138 adult coho salmon were used to prepare 32 composite samples for mercury analyses (Table 2-5). In addition, 38 yearling coho salmon were collected from 22 locations to create 8 composite samples, and 25 young (hatchery) coho salmon were collected directly from the Platte River hatchery, where the majority of Lake Michigan stocked salmon originate, and were used to create 5 composite samples.

Table 2-5. Number of Fish Collected by Species and Location

Species	Total Number of Individual Fish Collected	Number of Locations	Number of Composite Samples Created
Lake Trout	693	3	156
Coho salmon — adult	138	54	32
Coho salmon — yearling	38	22	8
Coho salmon — hatchery	25	1	5

2.4 Sampling Methods

Full details of the sampling methods used in the LMMB Study have been published by EPA in a methods compendium (USEPA, 1997d and 1997e). Field sampling for all media except sediment and fish adhered to strict protocols for the sampling of trace metals using "clean" techniques. Sampling personnel were outfitted with suits and gloves, "clean hands/dirty hands" techniques were employed, and pre-cleaned polytetrafluoroethylene bottles and equipment were used. "Clean" techniques were not used for the collection of sediments or fish, because these matrices were believed to contain significantly higher mercury concentrations, so contamination from background sources would be less of a concern. Brief summaries of the sampling procedures are provided below.

2.4.1 Atmospheric Components

2.4.1.1 Vapor Fraction

Vapor-phase mercury was quantitatively removed from air by amalgamation onto gold. Two gold-coated borosilicate glass bead traps in quartz tubing (with glass fiber pre-filters) were used in series. The traps were housed in a sampling box 3 m above the ground and maintained at 93 °C to prevent condensation. Samples were collected for 12-24 hours at flow rates of 10 to 30 L/min.

2.4.1.2 Particulate Fraction

Particulate atmospheric components were collected using a filter pack assembly containing pre-treated 47-mm glass fiber filters housed in custom-made sampling boxes. The volume of air sampled was measured with a calibrated dry test meter. The vacuum pumps attached to the sampling boxes were specially designed for trace level mercury sampling. The apparatus was deployed 3 m above the ground, and samples were collected for 12-24 hours at flow rates of 10 to 30 L/min.

2.4.1.3 Precipitation Fraction

Precipitation samples were collected by automated equipment that sensed the presence of precipitation and collected samples from each precipitation event during July 1994 to October 1994, and during each precipitation event from April 1995 to October 1995. Precipitation samples collected from November 1994 through March 1995 were collected on a weekly basis (e.g., each sample represented the precipitation that fell during all of that week). An automated sensor grid on the modified collector was activated by precipitation, causing the lid of the sampler to open for wet-only collection of precipitation samples. Samples were collected through a borosilicate funnel and in 1-L Teflon® bottles.

2.4.2 Tributaries

A small boat was anchored at the sampling site, above the centroid of the river. Water samples (500 mL) were collected from two depths (0.2 x river depth and 0.8 x river depth). Water was pumped through a Teflon® sampling tube (weighted with a Teflon® weight) and C-flex® pumphead tubing using a peristaltic pump. Dissolved samples were collected using in-line filtration. Mercury samples were preserved in the field with 10 mL of 50% HCl. Samples from the upper and lower depths were composited.

2.4.3 Open Lake

Open-lake samples were collected from various depths depending upon the stratification conditions. During stratification, open-lake stations were sampled at the mid-epilimnion and mid-hypolimnion. During non-stratified periods, samples were collected at mid-water column depth and two meters below the surface. Master stations, during times of non-stratification, were sampled at mid water column, one meter below the surface, and two meters off the bottom. During times of stratification, master stations were sampled at one meter below the surface, mid-epilimnion, mid-hypolimnion, and two meters off the bottom.

Teflon®-lined Go-Flo bottles were attached to Kevlar® lines with non-metallic weights. Two liters of sample were collected for total mercury analysis. Samples were aliquotted and filtered in a clean room onboard the ship. Particulate samples were collected onto 0.8-µm quartz fiber filters. Samples were frozen on board and shipped overnight to the laboratory.

2.4.4 Sediment

Sediment samples were collected from 118 stations in Lake Michigan using two types of equipment (Figure 2-5). Wherever sediments were sufficiently soft and fine grained to permit safe use of the box corer, the box corer was preferred for sampling. After retrieval of the box core, four subcores were taken from each box core. The subcore designated for radionuclide and mercury analyses was subsectioned at 1-cm intervals from top to bottom. The surficial 1 cm of each of these cores was analyzed for mercury. Box cores were collected from 51 stations during the study.

The second, and less preferred, method of collection was grab sampling using a Ponar sampler. Many sandy or stiff lake clay regions of sediment within the lake could not be box cored, so Ponar samples were collected at these locations. When retrieved, the Ponar was carefully drained and opened. The surficial 1-cm sediment layer was removed from the grab sample. If the surficial sediment layer contained less than 1 cm of recent sediment, then only the recent sediment was sampled. Recent sediment was visually identifiable from older sediments by changes in cohesiveness, color, and grain size. Older sediments were generally cohesive red-brown clays, whereas, recent sediments were brown to gray non-cohesive silty and clayey sands. In most instances, there was at least 1 cm of recent sediment. This surficial 1-cm layer was analyzed for mercury. Ponar samples were collected from 67 stations during the study.

Sediment traps were deployed at eight locations (Figure 2-6). The trap at Station 3, located in northern Lake Michigan (excluded from Fig. 2-6), was lost. Samples from the two traps at Station 6 had mercury chloride added as a preservative to their collection bottles prior to deployment and therefore were not analyzed. The trap at 245 m deep at Station 5 failed, and no sample was available from the trap at Station 4. Enough sample was available for mercury analysis from Stations 1, 2, 5, 7, and 8. Samples from two depths were available from Stations 7 and 8. Details of trap sampling can be found in Eadie (1997a, 1997b). All samples and subsamples collected were placed in polyethylene bags or bottles, immediately frozen on board the ship, and transported frozen to laboratory freezers (Edgington and Robbins 1997a).

2.4.5 Lower Pelagic Food Web Organisms

Phytoplankton were collected using a device called a phytovibe. This device was specially designed and constructed for GLNPO for collecting large volumes of plankton for analysis of chemical contaminants such as mercury and PCBs. The phytovibe consists of a pair of inverted pyramids constructed of stainless steel mesh lined with 10-µm Nitex netting. Water is pumped by a submersible pump through nylon tubing into the top of the device, which has an opening that is 1 m^2. The end of the nylon tubing is covered with 100-µm netting to remove zooplankton. In order to prevent plugging of the netting with plankton, the phytovibe is shaken by a motor. The samples were washed down into a detachable sampling cup with lake water and collected for processing. Sampling times ranged from 6 to 14 hours, depending on plankton concentration in the water and sample size needed for a particular analysis.

The depth of collection was chosen based on interpretations of the temperature, fluorescence, and turbidity profiles from the ship, with the objective of choosing a depth that maximized the occurrence of phytoplankton that were being grazed. This generally corresponded to the epilimnion or the subthermocline chlorophyll maximum in stratified conditions.

Zooplankton were collected in nested Nitex nets of two different mesh sizes (102-µm and 500-µm) during standard vertical tows, from near the bottom to the surface. The 500-µm nets were used to exclude larger organisms, including small fish, from the zooplankton samples. The number of tows performed was dependent on the mass of sample collected per tow. The required wet weight of material for mercury analyses was usually obtained in one or two tows.

2.4.6 Fish

Whole fish were collected intact, with all body fluids and no incisions, except lake trout, which had their stomachs removed. Fish were wrapped in aluminum foil, placed in polyethylene bags, tagged, and frozen onboard the vessel. The fish were aged by checking for coded wire tags on the head and for fin clips. Whole fish were then composited by age, location, species, and size range. Samples were homogenized using a 40-quart vertical cutter mixer for large fish, a 12-quart vertical cutter for medium sized fish, or a high-speed 2-quart cutter for small fish.

2.5 Analytical Methods

Full details of the analytical methods used in the LMMB Study have been published by EPA in a methods compendium (USEPA, 1997d and 1997e). Brief summaries of the specifics of the analyses for each lake component are provided in Sections 2.5.1 to 2.5.6. Except for the analyses of sediment samples, all of the other media used cold vapor atomic fluorescence spectrometry (CVAFS) instrumentation and sample preparation and analysis procedures that were similar to those described in EPA Method 1631 and Bloom and Fitzgerald (1988). The sediment sample analyses were conducted using cold vapor atomic absorption (CVAA) instrumentation.

2.5.1 Atmospheric Components

2.5.1.1 Vapor Fraction

The mercury collected on gold-coated glass beads was thermally desorbed from the traps at 500 °C and carried into a CVAFS analyzer.

2.5.1.2 Particulate Fraction

The glass fiber filters used to collect particulate atmospheric mercury were digested in 1.6 M nitric acid, using a microwave digestion procedure to release the mercury from the particulate material. The mercury in the digestate was then determined by oxidation with bromine monochloride, purge and trap, and CVAFS.

2.5.1.3 Precipitation Fraction

The mercury in precipitation samples was determined by oxidation with bromine monochloride, purge and trap, and CVAFS, without digestion.

2.5.2 Tributaries

Water samples from the tributaries were analyzed for mercury using the analytical techniques outlined in EPA Method 1631. Briefly, the mercury in a 100-mL sample aliquot was oxidized to Hg^{+2} with bromine monochloride. The sample was reduced with $NH_2OH{\cdot}HCl$ to destroy the free halogens, then reduced with stannous chloride ($SnCl_2$) to convert dissolved Hg^{+2} to volatile Hg^0. The Hg^0 was separated from solution by purging with an inert gas, collected onto a gold trap, and thermally desorbed from the trap into an inert gas stream that carried the Hg^0 into the cell of a CVAFS analyzer for detection.

Water samples were analyzed for methylmercury using a combination of distillation, ethylation, gas chromatography, and cold-vapor atomic fluorescence spectrometry. Briefly, methylmercury was distilled from a water sample with heat and a flow of inert gas. The distillate was treated with sodium tetraethyl borate, which converts the methylmercury to the more volatile methylethylmercury, which was separated on a gas chromatographic column. The methylethylmercury was pyrolyzed and converted to Hg^0, and swept into the CVAFS analyzer for determination of mercury.

2.5.3 Open Lake Water

Water samples from the open lake were analyzed for mercury using the same techniques described above for tributary samples.

2.5.4 Sediment

Sediment samples were freeze-dried in the laboratory in pre-weighed storage containers. The freeze-dried samples were stored in these containers until subsamples were removed for analysis. Samples were digested in one of two ways. Most surficial sediments were digested using a Leeman Labs, Inc., automated mercury system. The sediment trap samples and a few surficial sediment samples were digested using a 1.6 M nitric acid solution and a microwave digestion system (Uscinowicz and Rossmann 1997). The Leeman automated digestion uses 50% aqua regia and potassium permanganate solutions and provides a more vigorous digestion than the microwave procedure.

All samples were analyzed using a Leeman Labs, Inc. automated mercury analysis system. The analysis is based upon the cold vapor atomic absorption spectrophotometry (CVAAS) technique that reduces divalent mercury in solution to elemental mercury vapor using stannous chloride. Argon is used to carry the elemental mercury to the detector (Uscinowicz and Rossmann 1997).

2.5.5 Lower Pelagic Food Web Organisms

Freeze-dried plankton samples were placed in a PFA Teflon® digestion vessel with a 1:1 concentrated sulfuric acid and nitric acid mixture, then placed in a 70 °C hot water bath overnight. Mercury was determined by oxidation with bromine monochloride, purge and trap, and CVAFS.

2.5.6 Fish

Samples were digested in concentrated nitric acid by microwave digestion under high pressure and temperature. Mercury analysis was performed using CVAFS.

2.6 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The goal of the QA program was to ensure that all data gathered during the LMMB Study met defined standards of quality with specified levels of confidence. Data quality was defined, controlled, and assessed through activities that included development of study QAPPs, use of SOPs, and data verification. These activities are described in detail in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). Specific quality control elements implemented in the sampling and analysis of mercury included:

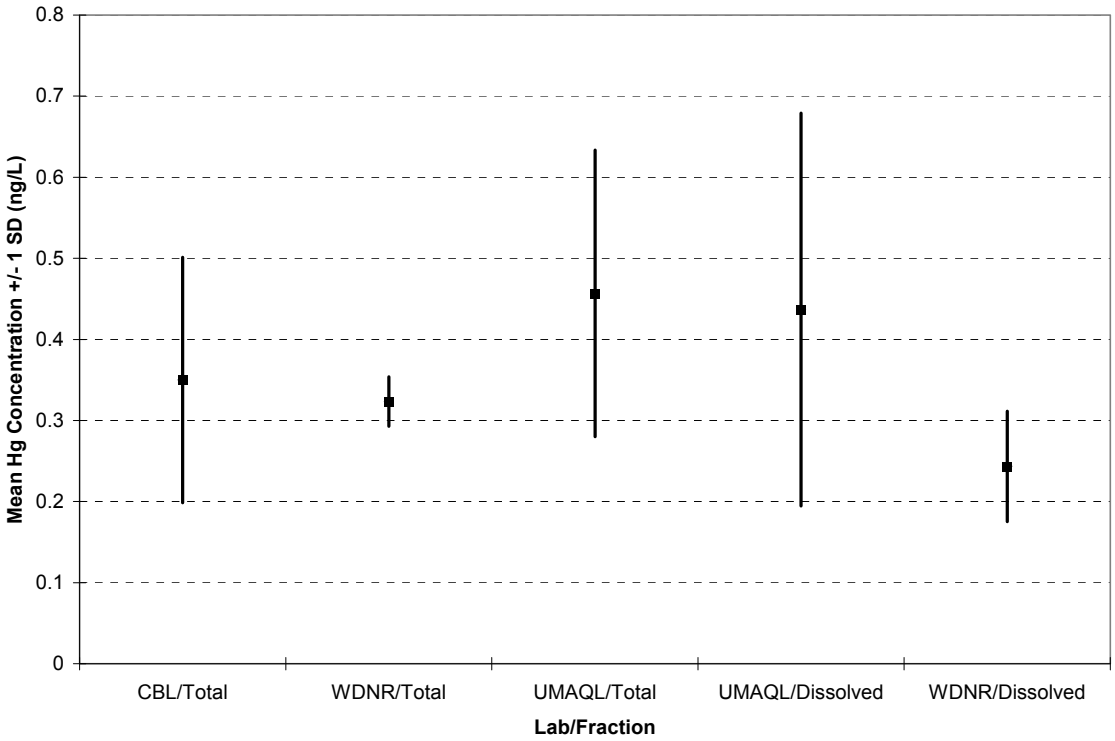
- use of standard operating procedures and trained personnel for field sampling and laboratory analysis;
- determination of method sensitivity through calculation of method detection limits;
- preparation and analysis of a variety of blanks to characterize contamination associated with specific sample handling, storage, and analysis processes including field blanks, lab reagent blanks, bottle blanks, trip blanks, and lab procedural blanks;
- collection and analysis of field or laboratory duplicate samples;
- analysis of standard reference materials;
- preparation and analysis of a variety of quality control samples including performance standards;
- use of a standardized data reporting format; and
- preparation and analysis of matrix spike samples to characterize the applicability of the analytical method to the study sample matrices.

In September 1995, GLNPO conducted an intercomparison study involving the mercury PIs at the Chesapeake Biological Laboratory (CBL), the University of Wisconsin Department of Natural Resources (WDNR), and the University of Michigan Air Quality Laboratory (UMAQL). The performance of these three laboratories could be more readily compared because they were analyzing similar sample matrices, e.g., river water, lake water, and precipitation. The performance of the laboratories analyzing the plankton, fish, and sediment samples could not be compared in a similar fashion, given the significant differences in the sample preparation procedures used for each of these matrices. The study compared the submersible pump collection technique performed by Gerald Keeler (University of Michigan) and the Go-Flo bottle technique performed by Robert Mason (University of Maryland's Chesapeake Biological Laboratory). Drs. Keeler and Mason collected samples from the same point aboard the *R/V Lake Guardian*. Dr. Hurley collected samples from an inflatable boat rowed several hundred yards from *R/V*

Lake Guardian. Each of the PIs analyzed the samples in triplicate using the cold vapor atomic fluorescence techniques described in Section 2.5.

The results are shown in Figure 2-8. The laboratory and sample fraction (total mercury vs. dissolved mercury) are shown on the x-axis. The vertical bars represent the mean mercury concentration ± one standard deviation for each laboratory/fraction combination. The Chesapeake Biological Laboratory only provided data for total mercury. The mean total mercury concentrations from all three laboratories agree within a factor of 1.4. The mean dissolved mercury concentrations from the two laboratories that submitted dissolved mercury data agree within a factor of 1.8.

Figure 2-8. Results from Intercomparison Study of Three LMMB Laboratories Analyzing Mercury in Aqueous Samples



In addition to the intercomparison study, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data. Prior to data submission, each researcher submitted electronic test files containing field and analytical data according to the LMMB data reporting standard. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers.

Prior to sample collection, quality assurance project plans (QAPPs) were developed by the PIs and submitted to GLNPO for review. In the QAPPs, the PIs defined measurement quality objectives (MQOs) in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. The MQOs were designed to control various phases of the measurement process and to ensure that the total measurement uncertainty was within the ranges prescribed by the DQOs. The MQOs for mercury are listed in Section 5 of *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b).

The PI-defined MQOs also were used in the data verification process. GLNPO conducted data verification through the LMMB QA Workgroup. The workgroup was chaired by GLNPO's Quality Assurance Manager and consisted of quality control coordinators that were responsible for verifying the quality of specific data sets. Data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. If the results failed to meet MQOs and corrective actions were not feasible, the results were flagged to inform data users of the failure. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. In addition, a wide variety of flags were applied to the data to provide detailed information to data users. For example, the flag LAC (laboratory accident, no result reported) was applied to sample results to document that a sample was collected, but no result was reported due to a laboratory accident. The frequencies of flags applied to mercury study data are provided in the Quality Implementation Sections of each of the following chapters. The flag summaries include the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but do not include all flags applied to the data to document sampling and analytical information (such as LAC). In order to provide detailed quality information to data users, the study data are maintained in the GLENDA database with all applied flags. Detailed definitions of the flags can be found in the Allowable Codes Table on GLNPO's website at: www.epa.gov/glnpo under Result Remark, List of QC flags (lab_rmrk).

The PIs participating in the study also conducted real-time data verification. PIs applied best professional judgement during sampling, analysis, and data generation, based on their experience monitoring mercury in the environment. In most cases, when sample results were questionable, the PI reanalyzed the sample or clearly documented the data quality issues in the database through the application of data quality flags or by including comments in the database field, "Exception to Method, Analytical." Because the flags and comments are maintained in the database for each sample result, data users are fully informed of data quality and can evaluate quality issues based on their intended use of the data. The level of documentation that GLNPO is maintaining in the study database is unprecedented for a database of this size and will serve as a model for future efforts.

GLNPO also conducted data quality assessments in terms of three of the six attributes used as the basis for the MQOs, specifically sensitivity, precision, and bias. For example, system precision was estimated as the mean relative percent difference (RPD) between results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD between results for laboratory duplicate pairs. Bias was estimated using the mean recovery of spiked field samples or other samples of known concentration such as laboratory performance standards. A summary of data quality assessments is provided for the mercury study data in the Quality Implementation Section of each of the following chapters.